Oxidative Dehydrogenation of Cyclohexane on Cobalt Oxide (Co_3O_4) Nanoparticles: The Effect of Particle Size on Activity and Selectivity

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The catalytic dehydrogenation of cyclohexane is a critical step in the reforming of naphtha, and in addition, important in the commercial production of benzene where significant quantities of cyclohexane that remain in the product stream must be removed at a considerable expense[1]. The proper application of nanoparticles in catalytic systems has provided a unique ability to tailor catalytic materials in ways previously unforeseen; and as such, interest has developed in the application of cobalt and cobalt oxides as an alternative catalyst for noble metals. For example, investigations of cobalt nanoparticles determined a strong metal-support effect for oxidized Co_{27} in the oxidative dehydrogenation of cyclohexene[2]. In this work we investigate the catalytic properties of 3-7nm vs. 8-15nm Co_3O_4 nanoparticles deposited on ALD formed Al_2O_3 supports with respect to cyclohexane oxidative dehydrogenation to benzene.

The Co_3O_4 3-7nm and 8-15nm particles were formed through a surfactant free preparation utilizing $Co(CH_3COO)_2x4H_2O$ and ammonia as the starting material (by the Flytzani-Stephanopoulos group at Tufts University). Temperature programmed reaction (TPRx) was performed in combination with *in-situ* grazing incidence small angle x-ray scattering (GISAXS) and grazing incidence x-ray absorption spectroscopy (GIXAS) investigations at the Sector 12-ID-C Beam Line of the Advanced Photon Source at ANL to study catalytic activity while observing changes in morphology and chemical state[3]. The GISAXS analysis found reorganization to occur in groups of particles yet no further agglomeration to larger sizes or sintering while GIXAS showed the 8-15nm particles began with a mixed CoO and Co_3O_4 phase that aged to become entirely Co_3O_4 in nature after heating in an oxygen rich environment. TPR_x analysis determined the 3-7nm particles were more active for the creation of benzene as the turnover rate was 5 times greater than the 8-15nm particles with the greatest activity occurring at 300°C.

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